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Session 10F: Combustion

The Effect of Diesel Particle Filters and Selective Catalytic Reduction - A Predictive Framework for Ultrafine Particle Formation, Toxicity and Chemical Composition

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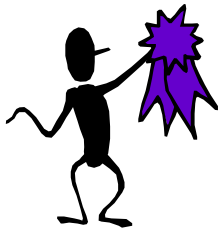
California Air Resources Board

California Environmental Protection Agency
Air Resources Board



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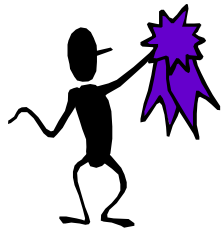

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USC: Prof. Constantinos Sioutas, Vishal Verma, Harish Phuleria

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ELK GROVE Unified School District

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CALIFORNIA DEPARTMENT OF TRANSPORTATION

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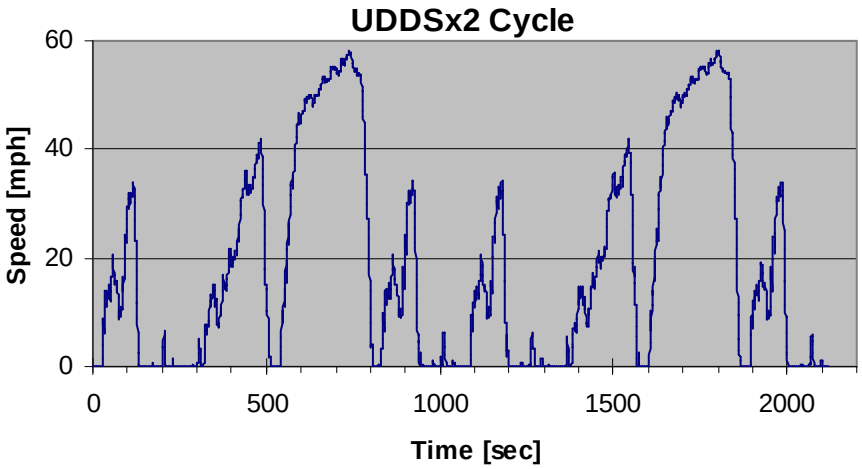
Experimental Setup

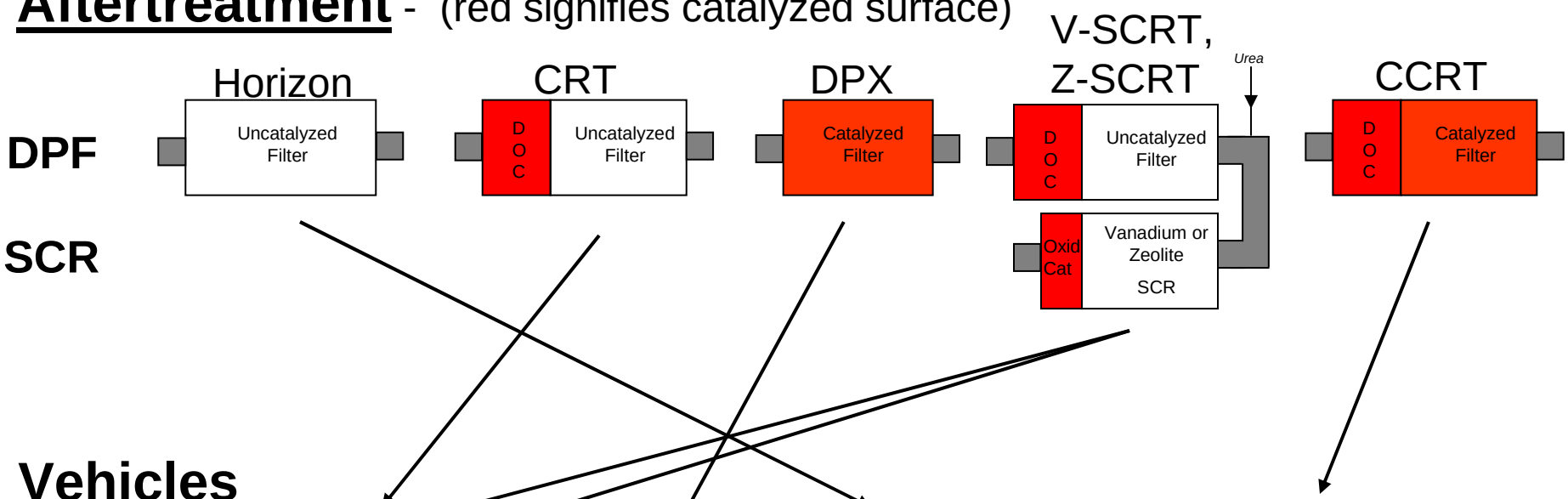
CARB Heavy duty Diesel Emissions Test Laboratory

- **Ultra Low Sulfur Diesel (6ppm)**
- **CVS - Dilution Tunnel**
- **Real time particle measurements:**
  EEPS, DMS500, SMPS, CPC's, DC, PAS
- **Cycles:**
  Cruise at 50mph, UDDSx2, Idle



Test Matrix
4 vehicles, 6 configurations + Baseline

Aftertreatment - (red signifies catalyzed surface)



Vehicles

Veh#1

1998 Cummins Diesel
11L, 360,000 miles

Veh#2

1999 International Diesel
7.6L, 40,000 miles

Veh#3

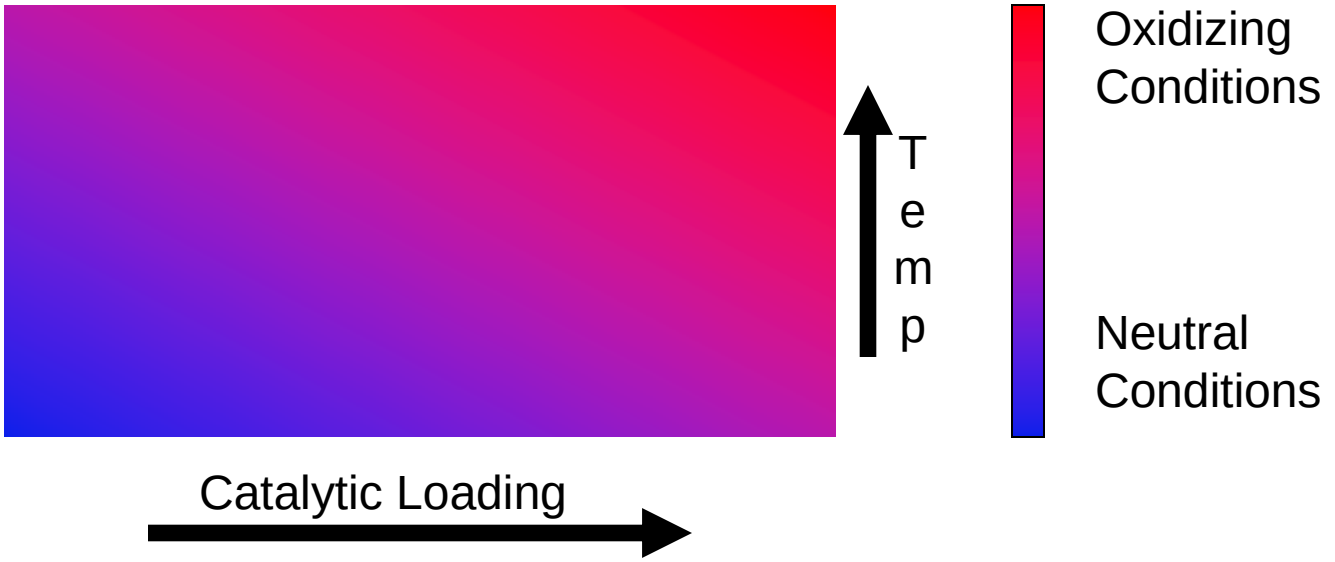
2003 Cummins Diesel
5.9L, 50,000 miles

Veh#4

2006 Cummins Diesel w/ Allison
Hybrid drive. 5.9L, 1,000 miles

Aftertreatment as Chemical Reactors

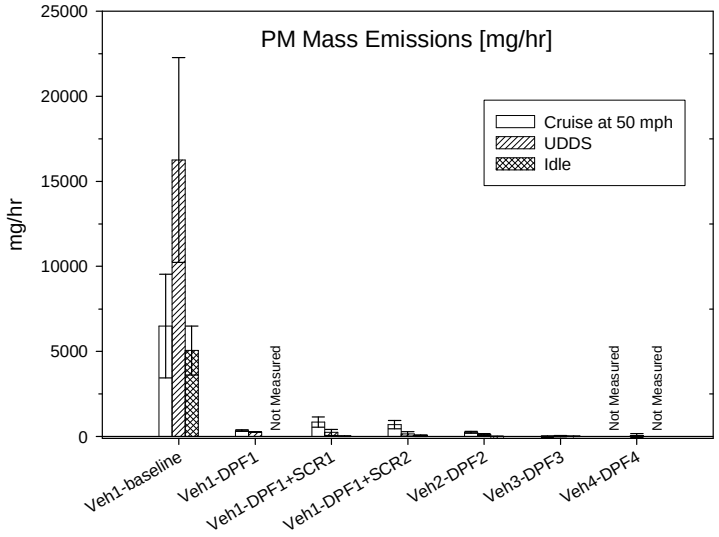
A Predictive Framework - Redox Chemistry

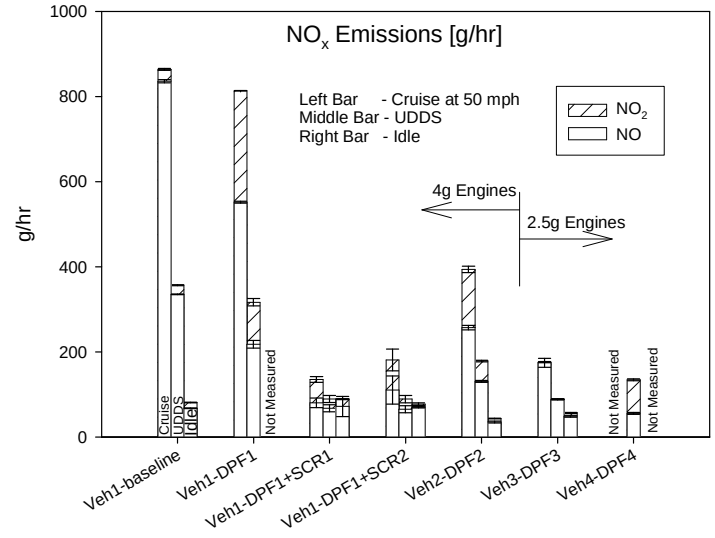


Oxidation of Diesel Exhaust

- **Organics (OC, THC, PAHs)** ↓
- **CO** ↓
- **NO_2/NO_x** ↑
- **$SO_2 \rightarrow SO_3 \rightarrow$ nucleation** ↑

Aftertreatment *Significantly* Reduces PM and NO_x



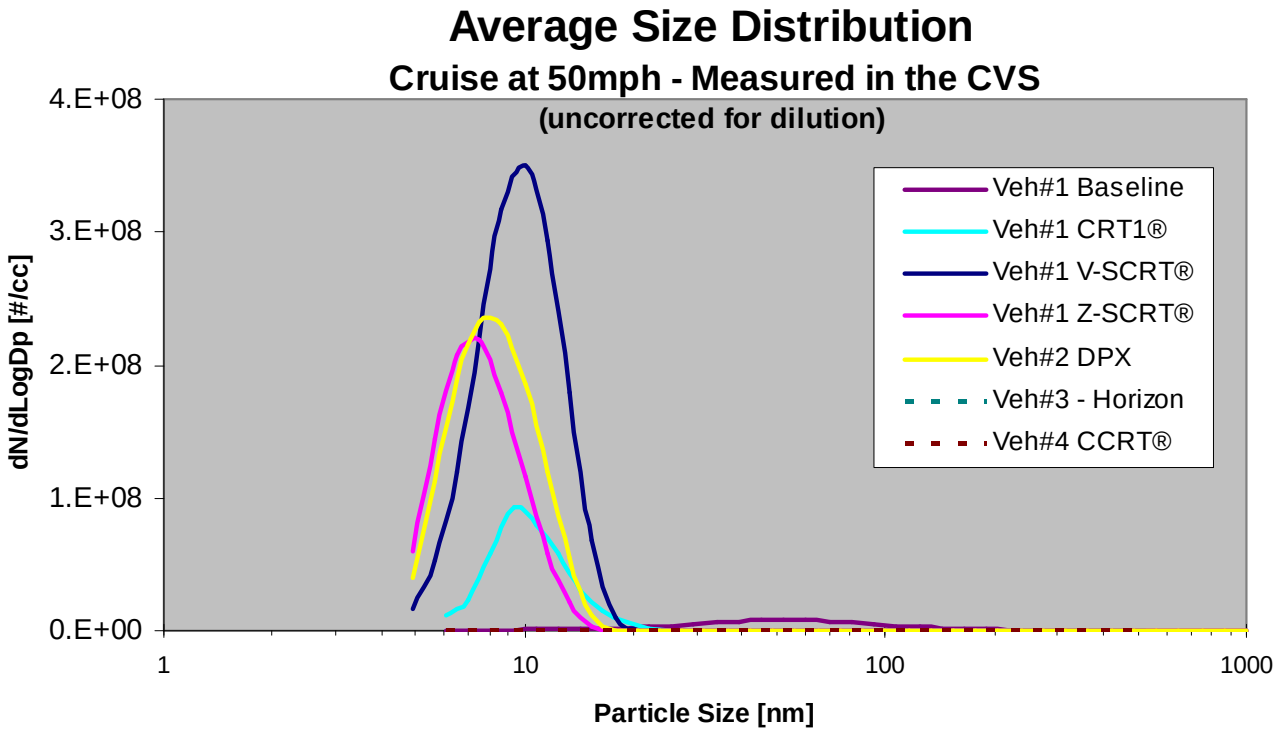


PM Mass Reductions of 95%+
(not temperature or cycle dependent)

NO_x Reductions of 75%+
(dependent on temperature, i.e. duty cycle)

Herner et al., *ES&T* **2009**, *43* (15), pp 5928–5933

Nucleation

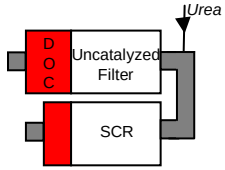


- $SO_2 \rightarrow SO_3 \rightarrow$ Nucleation (water or ammonia)
- Storage

<u>Accumulation mode seen in:</u>
Veh#1 Baseline

<u>Nucleation mode seen in:</u>
Veh#1 CRT

Veh#1 V-SCRT
Veh#1 Z-SCRT

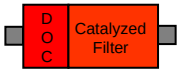


Veh#2 DPX

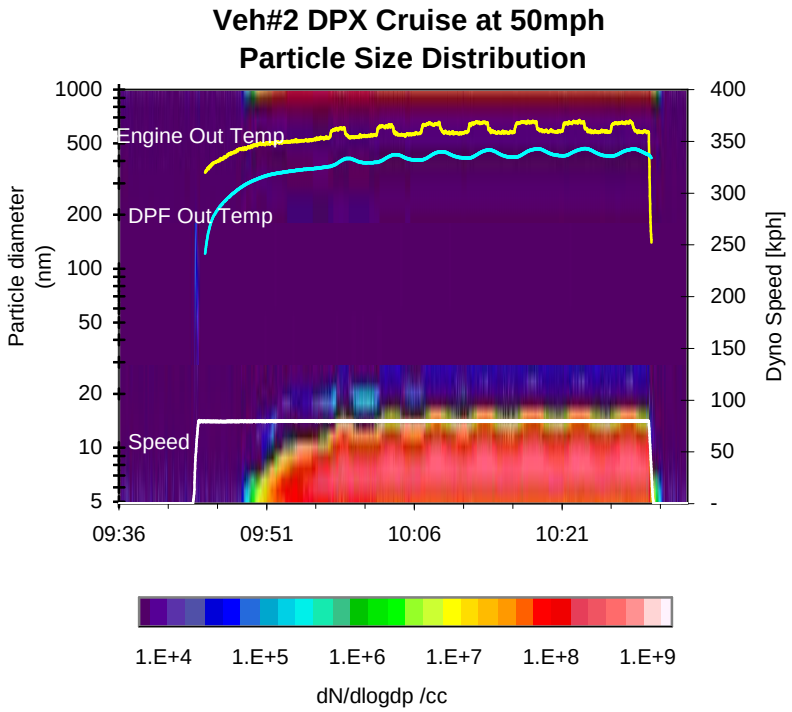
<u>No nucleation mode in</u>
Veh#1 Baseline

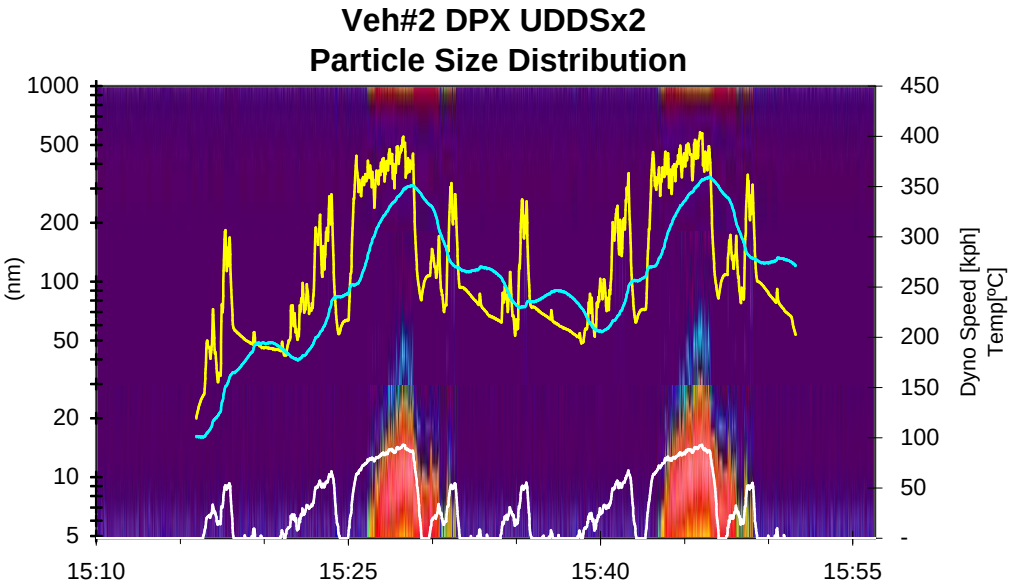
Veh#3 Horizon

Veh#4 CCRT



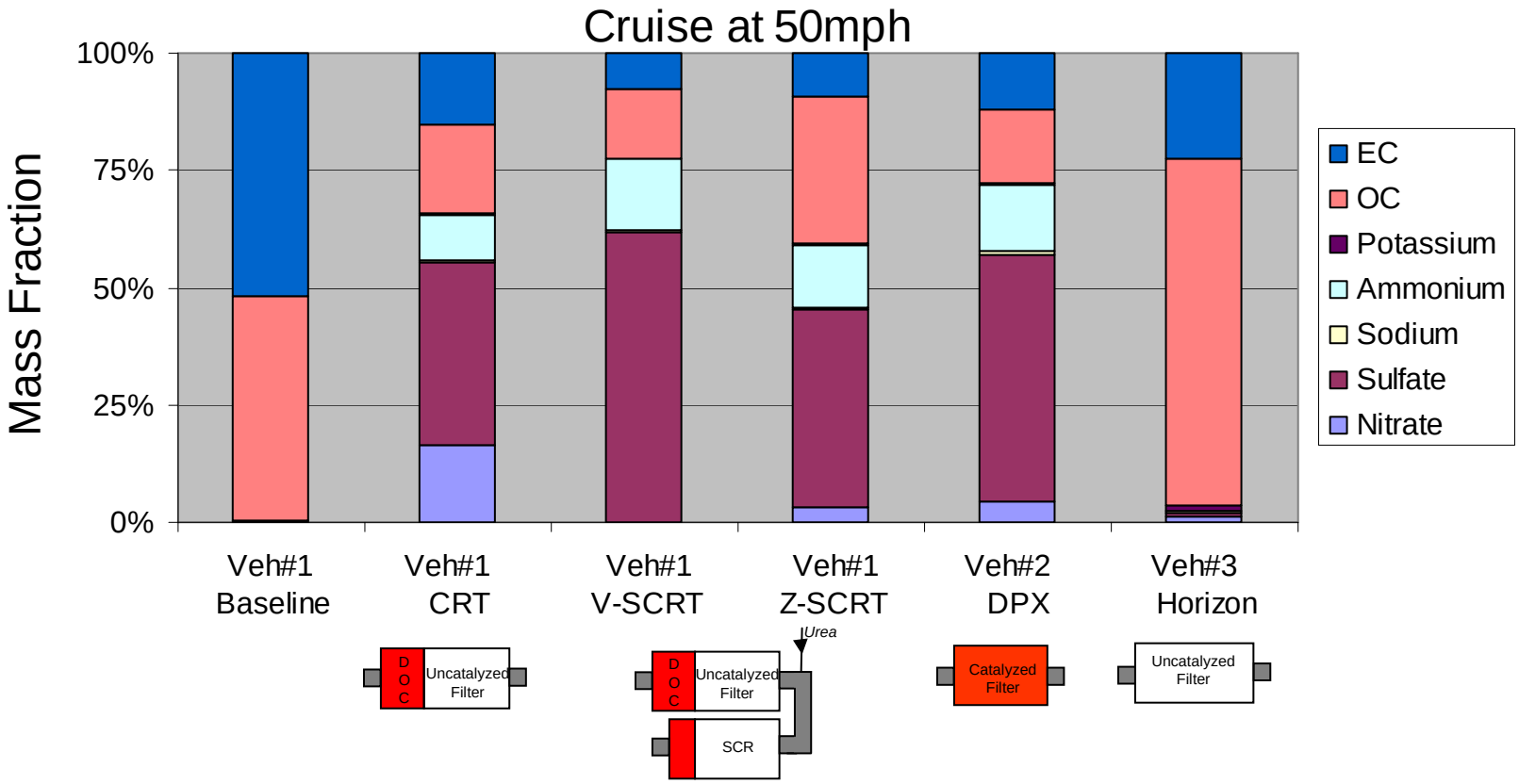
Nucleation





Nucleation occurs when a *threshold* temperature has been reached leading to sulfation

Chemical Composition of PM



- Baseline PM – 50% OC 50% EC
- Nucleating Aftertreatment – Majority Ions such as Sulfate and Ammonium
- Non Nucleating Aftertreatment – Still mostly OC with some EC
  - (DPF preferentially filters EC)

IN VITRO TEST FOR THE TOXICITY OF PARTICULATE MATTER

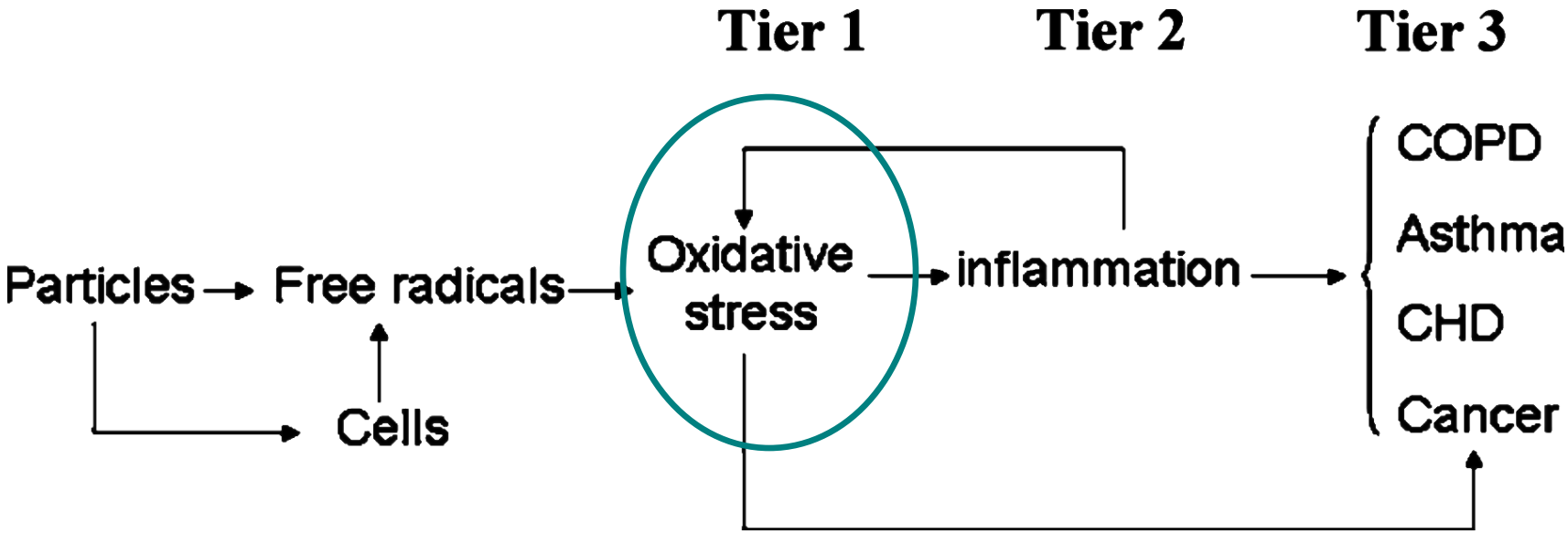
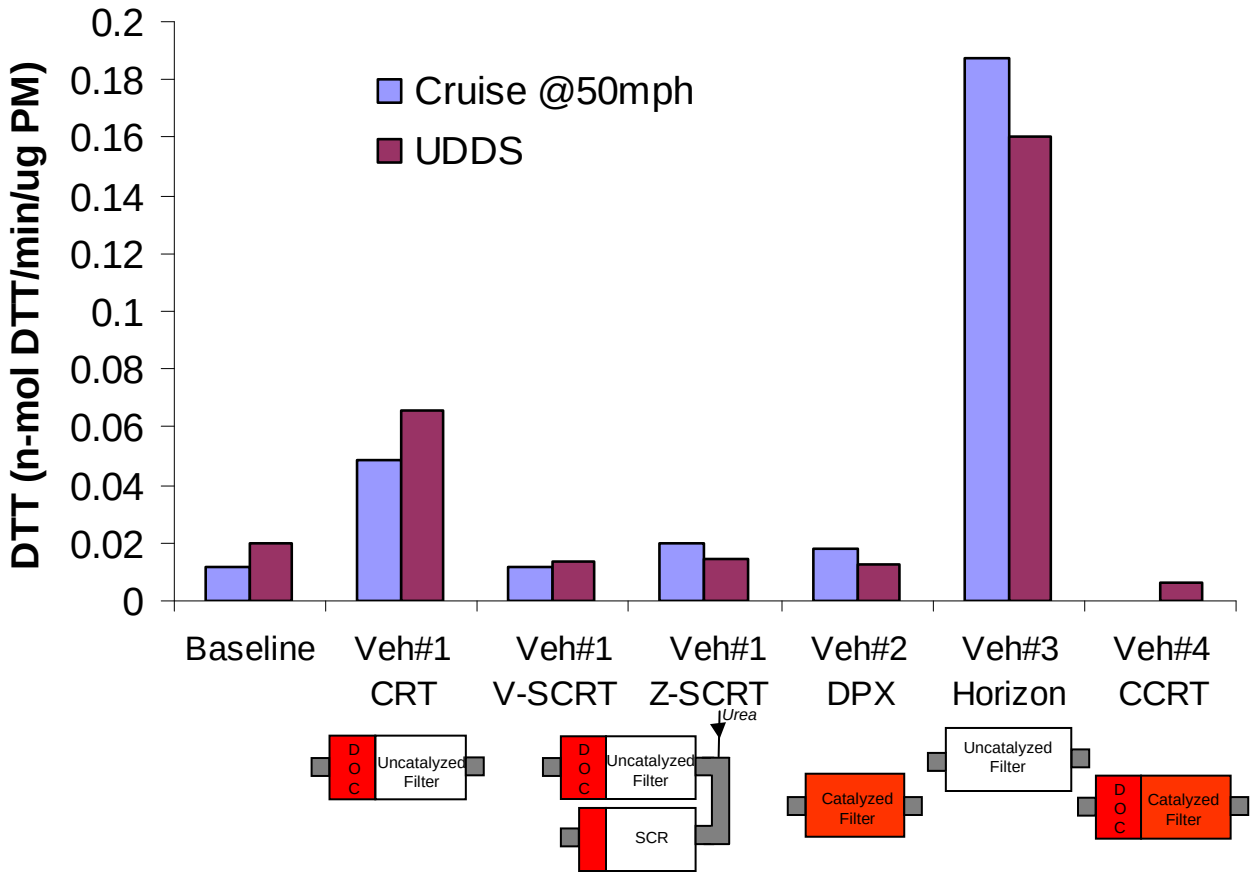


FIG. 1. Schematic of disease induction pathway from particle exposure. (Ref: J. G. AYRES ET AL. Inhalation Toxicology, 20:75–99, 2008)

- **Measurement of Oxidative Stress Potential**
  - ***in vitro toxicity test***
    - **Acellular systems (DTT) / Cellular systems (macrophage cell, DCFH-DA)**

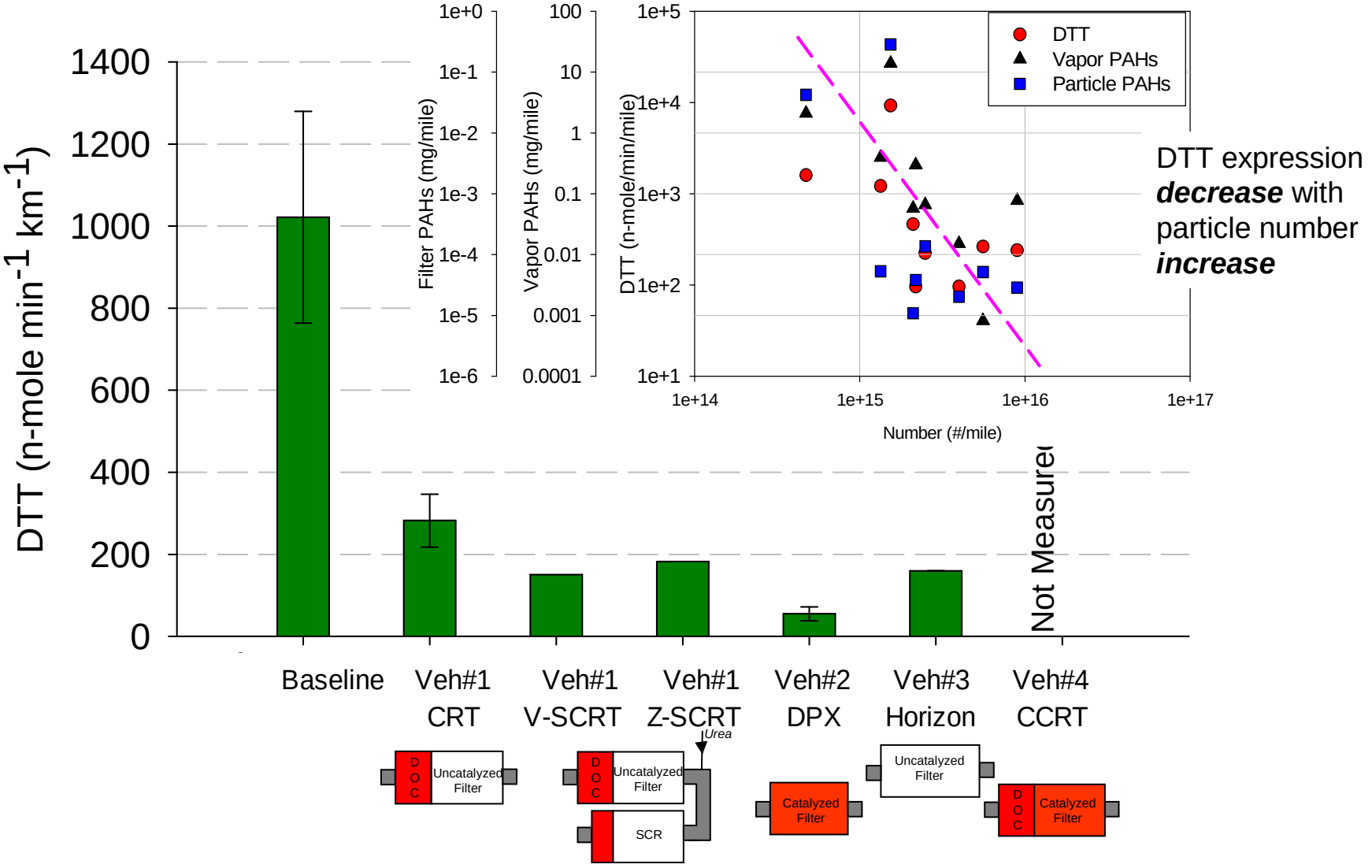
OXIDATIVE STRESS POTENTIAL OF TOTAL PM PER PM MASS



- **DTT highly correlated with water-soluble organic carbon (WSOC)***
- **Uncatalyzed filters better at filtering EC than WSOC**
- **Catalyzed aftertreatment reduces WSOC**

*Biswas et al., ES&T, **2009**, *43* (10), pp 3905–3912

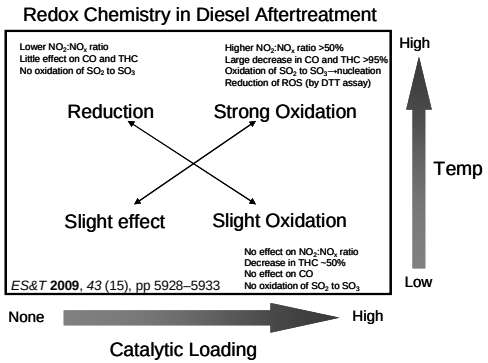
OXIDATIVE STRESS POTENTIAL OF TOTAL PM PER DISTANCE DRIVEN IS REDUCED BY ALL HD RETROFITS



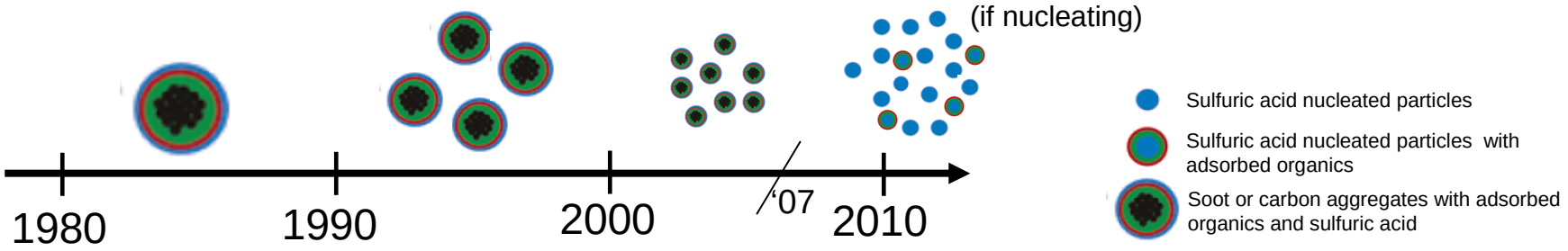
DTT expression ***decrease*** with particle number ***increase***

Conclusions

- **The decrease of diesel PM and NO_x with the advent of DPFs and SCR will greatly improve air quality in California.**
- **Secondary effects of diesel aftertreatment are becoming better understood:**
  - Oxidation of exhaust is a function of catalytic loading and exhaust temp.
  - As NO_2/NO_x and particle number increase, organics (THC, PAH's, WSOC, etc), CO and DTT expression decrease.



- **Not all Ultrafine particles are the same**
  - Nucleation mode particles, when present, post aftertreatment are morphologically, chemically and toxicologically different from traditional diesel exhaust particles.



Next Steps

- Effect of toxicity in other assays forthcoming
- Current study based on *passive retrofit* or pre-2010 technology.
- It will be important to test 2010 OEM technology, as effect may be different from what is described here.

Thank you